

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF EASILY DISPERSIBLE PIGMENTS OF THE β -MODIFICATION OF PHTHALOCYANINE

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of easily dispersible pigments of the β -modification of phthalocyanine.

It is known that the β -modification of copper phthalocyanine (CuPc) which has been prepared by condensation according to the phthalic acid anhydride process and which, if desired, has been extracted with dilute acid, can be brought into the pigment form by means of various methods of fine dispersion. Preferred methods are grinding with salt in the presence of additives preventing a phase transformation or grinding in organic solvents. The products obtained according to these processes have sufficient tinctorial strength, but, the shade and purity thereof as well as various technical properties must be improved. For this purpose, the crude pigment containing impurities must be purified. The German Offenlegungsschriften Nos. 2,262,911 and 2,262,895 describe processes according to which the crude pigment is converted into the CuPc-sulphate with sulphuric acid to dissolve the undesired impurities, the CuPc-sulphate separated, the pure sulphate hydrolyzed and the pure CuPc isolated.

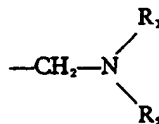
The α -modification of the pure CuPc thus obtained is rearranged into the β -modification according to known methods, for example by a thermal treatment or by the action of aromatic solvents. When the β -modification of the highly pure CuPc of these purification and rearrangement processes is finely dis-

persed according to a known mechanical process, for example solvent grinding, pigments are unexpectedly obtained that do not have any colouristic interest because of their dull shade and extreme lack of tinctorial strength.

This invention is based on the observation that easily dispersible phthalocyanine pigments of the β -modification of high tinctorial strength and high stability towards flocculation can be obtained when the β -modification of a highly pure copper phthalocyanine is subjected to a mechanical fine dispersion in the presence of compounds of the general formula

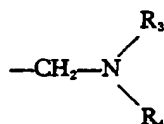


in which Pc represents a phthalocyanine radical, A represents an identical or different group of the formulae $-\text{COOM}$ or SO_3M (M being a hydrogen atom or one molar equivalent of an alkali metal ion, an alkaline-earth metal ion or an ammonium ion, or a carbamoyl, sulphamoyl, or N - alkylcarbamoyl group containing 1 to 12 carbon atoms, an N - alkylsulphamoyl group containing 1 to 18 carbon atoms, an N,N - dialkylsulphamoyl group, each alkyl having 1 to 4 carbon atoms, N - (2 - aminoethyl) - sulphamoyl, N - benzylsulphamoyl, N - phenylethylsulphamoyl, N - cyclohexylsulphamoyl, an N - alkyl - N - cyclohexylsulphamoyl group having 1 to 4 carbon atoms in the alkyl radical, an N - phenylsulphamoyl or an N - alkyl - N - phenylsulphamoyl group containing 1 to 4 carbon atoms in the alkyl radical group, a carboalkoxy group having 1 to 4 carbon atoms in the alkoxy radical, a sulphonic acid phenyl ester or sulphonic acid alkyl ester group containing 1 to 4 carbon atoms or an aminomethyl group of the formula

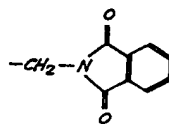


in which R_1 represents a hydrogen atom, an alkyl group having 1 to 18 carbon atoms, a 2-aminoethyl, benzyl, phenylethyl, phenyl, alkylphenyl or alkanoyl group each having 1 to 4 carbon atoms in the alkyl radicals, or a benzoyl group, R_2 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms or R_1 and R_2 together represent a phthaloyl group and $m=1$ or 2, provided that A is a group of the formula $-\text{SO}_3\text{M}$, or $m=1, 2, 3$ or 4, provided that A represents one of the sulphonoyl or sulphonic acid groups mentioned above, or $m=1, 2$ or 3, provided that A represents a $-\text{COOM}$ group, one of the carbamoyl or carboxylic acid ester groups or $m=\text{an integer of from 1 to 6}$, preferably from 2 to 4, provided that A is one of the aminomethyl groups mentioned above.

Preferred additives of the formula I are compounds in which A are identical or different groups of the formula $-\text{COOH}$ or $-\text{SO}_3\text{H}$ and their alkali metal, calcium, barium or ammonium salts, sulphonoyl, alkylsulphonoyl groups having 1 to 18 carbon atoms, N,N -dialkylsulphonoyl groups each alkyl radical having 1 to 4 carbon atoms, N -(2-aminoethyl)-sulphonoyl, N -benzylsulphonoyl, N -phenylethylsulphonoyl, N -cyclohexylsulphonoyl, N -alkyl- N -cyclohexylsulphonoyl groups having 1 to 4 carbon atoms in the alkyl radical, N -phenylsulphonoyl, N -alkyl- N -phenylsulphonoyl groups having 1 to 4 carbon atoms in the alkyl radical, carbamoyl groups, sulphonic acid phenyl ester or aminomethylene groups of the formula



or



in which R_1 is an alkyl group having 1 to 18 carbon atoms, a phenyl or an alkylphenyl group having 1 to 4 carbon atoms in the alkyl radical, R_3 and R_4 each represents an alkyl group having 1 to 4 carbon atoms, m being 1 or 2, provided that A stands for $-\text{COOH}$, $-\text{SO}_3\text{H}$, their salts or a carbamoyl group, m being 2 or 3, provided that A is one of the sulphonic acid amide or sulphonic acid ester groups and m being 2 to 4, provided that A is an aminomethyl group.

Suitable phthalocyanines of the general formula I are metal containing or metal free compounds, preferably copper phthalocyan-

ines which may carry further substituents in addition to the substituents A, for example copper phthalocyanine carboxylic acids, especially CuPc - monocarboxylic acid, -dicarboxylic acid and mixtures thereof; alkali metal, alkaline earth metal or aluminium salts of CuPc - carboxylic acids, salts of CuPc - carboxylic acids with ammonia or aliphatic amines; copper phthalocyanine sulphonic acids and CuPc - sulphonic acid mixtures, especially copper phthalocyanine monosulphonic acid; alkali metal and alkaline earth metal salts of copper phthalocyanine sulphonic acid, especially of copper phthalocyanine monosulphonic acid; salts of CuPc - sulphonic acids with ammonia or aliphatic amines; copper phthalocyanine carbamoyls, preferably those in which $m=1$ to 2 which may be alkylated with alkyl groups containing 1 to 18 carbon atoms; copper phthalocyanine carboxylic acid esters; copper phthalocyanine sulphonoyls, preferably those in which $m=2$ to 3 which may be obtained by reacting CuPc - sulphonoyl chlorides with ammonia or primary or secondary aliphatic, cycloaliphatic, aromatic or mixed aliphatic-aromatic amines, for example, methylamine, hexylamine, α -ethylhexylamine, dodecylamine, stearylamine, diethylamine, di- n -butylamine, cyclohexylamine, ethylenediamine, aniline, N -methyl-aniline, benzylamine or phenyl-ethylamine; copper phthalocyanine sulphonic acid esters, for example alkyl esters or aryl esters; alkylaminomethyl or dialkylaminomethyl copper phthalocyanines, preferably those in which $m=2$ to 4, which may be obtained by reacting chloromethylated copper phthalocyanines with primary or secondary aliphatic amines, for example methylamine, butylamine, hexylamine, octylamine, dodecylamine, stearylamine, di- n -butylamine or ethylene diamine; arylaminomethyl or alkylarylamino-methyl copper phthalocyanines, preferably those in which $m=2$ to 4 or phthalimido-methyl copper phthalocyanines, preferably those in which $m=2$ to 4 and which may be obtained by reacting copper phthalocyanines with N -methylolphthalimide.

Except for other definitions, "alkyl" and "alkanoyl" are to be understood as groups which contain from 1 to 4 carbon atoms in the alkane radical, "aryl" is preferably "phenyl" and "cycloalkyl" means groups having 4 to 8, preferably 6 carbon atoms.

The term " β -modification of highly pure copper phthalocyanine" is to be understood to mean products which have been purified according to the methods described in German Offenlegungsschriften Nos. 2,262,911 and 2,262,895 and rearranged into the β -modification according to known methods.

German Offenlegungsschrift No. 2,262,911 relates to a process for the preparation of the α -modification of highly pure copper phthalocyanine pigments which process comprises

5 converting unsubstituted or substituted, preferably halogenated, especially chlorinated (above all those having a chlorine content of up to 6%) copper phthalocyanines having different degrees of purity by means of suitable acids which dissolve the impurities contained in the pigment, preferably sulphuric acid, into copper phthalocyanine salts capable of being isolated, separating them from the acid, setting free from the copper phthalocyanine salts by the action of water the α -modification of the copper phthalocyanines in pure form and subjecting the isolated copper phthalocyanines in an aqueous suspension to a mechanical fine dispersion. The starting material is preferably dissolved in sulphuric acid or oleum and the solution diluted to a concentration of acid down to 80% by adding water or dilute sulphuric acid or the crude material is introduced into 80 to 86% sulphuric acid.

10 German Offenlegungsschrift No. 2,262,895 relates to a process for the purification of unsubstituted or substituted preferably halogenated, especially chlorinated (above all those having a chlorine content of up to 6% by weight) copper phthalocyanines which comprises introducing the copper phthalocyanine into 84 to 88% sulphuric acid or dissolving it first in concentrated sulphuric acid or oleum and then adjusting it with water or dilute sulphuric acid to the concentration mentioned, subjecting the copper phthalocyanine sulphate so formed at 60–100°C, preferably 70–90°C, in an inert gaseous atmosphere, preferably nitrogen, to a process of crystal growth, isolating the copper phthalocyanine sulphate and recovering the copper phthalocyanine by the action of water. The sulphuric acid is preferably used in 4 to 15 times the amount calculated on the weight of the starting material, and the crystal growth process is preferably carried out at a concentration of sulphuric acid of 85.5% to 86.5%.

15 The amount of a compound of the general formula I used is in general within the range of from 2 to 15% by weight calculated on the β -modification of the CuPc.

20 The amount required for obtaining an optimum pigment depends on the chemical constitution of the additive. When CuPc-sulphonic acids are used, the most favourable amount is within the range of 3 to 6% by weight, in the case of the CuPc-carboxylic acids of 5 to 8% by weight, and in the case of the other compounds of the general formula I of 4 to 10% by weight.

25 The preparation of an effective mixture of the β -modification of the pure CuPc with an added compound of the general formula I is advantageously carried out by the process of fine dispersion required for the conditioning to the pigment, in which case the compounds of the general formula I can be added

at the beginning or during the process of the fine dispersion. 65.

In principle, the pure CuPc of the β -modification and compounds of the general formula I can be finely dispersed separately and the ground suspensions mixed afterwards. The mixture of finely dispersed β -phase of pure CuPc and finely distributed additives of the general formula I in the form of dry pigment powders, however, yields pigments of less satisfactory properties. 70

When CuPc-carboxylic acids which are very important as additives of the general formula I are used, an especially economical process for the preparation of the mixture is the synthesis of CuPc containing the desired amount of CuPc-carboxylic acids by co-synthesis starting from phthalic acid anhydride and a small amount of trimellitic acid or other suitable benzene polycarboxylic acid according to the phthalic acid anhydride process. 75

The products so synthesized when purified with sulphuric acid and rearrangement of the phase yield the starting products required for the mechanical fine dispersion. When other CuPc-derivatives of the general formula I are used, that type of co-synthesis is not expedient. 80

When CuPc-sulphonic acids are used as additives, a separate synthesis is not necessary, since during the purification of the CuPc reprecipitation from sulphuric acid the CuPc can be partially sulphonated. The added CuPc-sulphonic acids and CuPc-carboxylic acids can be converted into the salts mentioned during or after the fine dispersion by reacting them with bases or with amines. 85

Suitable mechanical fine distribution processes are the generally known ones, for example salt grinding in mills or kneaders preferably grinding in a liquid grinding medium in a roller mill, a vibration mill, a bead mill or a stirrer ball mill with the aid of the grinding bodies and under the conditions generally used in practice. 90

Suitable grinding media are above all organic liquids and mixtures of water with organic liquids. Water can be used only to a limited extent because of partial rearrangement into the γ -phase. Suitable organic liquids are aliphatic and aromatic compounds. When aromatic liquids are used, for example xylene, a prior rearrangement of the γ -phase of the purified CuPc can be dispensed with because the use of such grinding media brings about the rearrangement of phases into the β -phase, the mixture with an additive and the fine dispersion being carried out in a single-step operation. 95

Preferred mixtures of water with organic liquids are homogeneous mixtures of water with primary, secondary or tertiary aliphatic alcohols having from 1 to 6 carbon atoms. Should coarser grains be required for predetermined application fields, an after-treat- 100 105 110 115 120 125

ment of the ground pigment in organic or aqueous-organic media at elevated temperature may be advantageous. The pigments are isolated according to known methods, preferably by evaporation or spray-drying.

The pigments prepared according to the process of the invention are suitable for colouring lacquers, paper, plastics and synthetic resins, synthetic fibres in the mass, and for printing paper, textiles, films and sheets and other materials and for metal effect lacquerings as well as paints.

The addition of the above-mentioned phthalocyanine derivatives of the general formula I to phthalocyanines has been described in U.S. Patents Nos. 2,526,345 and 3,028,392 and in German Patent No. 1,239,270. The pigment mixtures described therein show an improved stability towards flocculation, but they have a low tinctorial strength and bad dispersibility. In comparison therewith, the addition of these phthalocyanine derivatives to highly pure phthalocyanine yields pigments having a clear shade and distinctly improved dispersibility and tinctorial strength.

The following Examples illustrate the invention, the parts and percentages being by weight.

EXAMPLE 1

For the preparation of copper phthalocyanine which contains about 8% of copper phthalocyanine carboxylic acid (calculated on the pure pigment), 1400 parts of nitrobenzene, 740 parts of phthalic acid anhydride, 21 parts of trimellitic acid, 1170 parts of urea, 85 parts of ammonium chloride, 240 parts of anhydrous copper sulphate and 1 part of ammonium molybdate were mixed and heated to 200°C within 8 hours while stirring. The mixture was then stirred at 200°C for 4 hours and after turning off the heating, 200 parts of nitrobenzene were added. The suspension was cooled to room temperature, filtered and washed with nitrobenzene; the filter cake was washed with methanol and then with water. The moist filter cake was introduced into a mixture of 2000 parts of water and 1000 parts of concentrated hydrochloric acid, stirred at 90°C for 5 hours, filtered and washed with water until neutral. The filter cake was dried at 100°C. 716 parts of a 93% crude copper-phthalocyanine were obtained that contained about 8% of copper phthalocyanine carboxylic acid (calculated on the pure pigment).

For the preparation of the pure pigment, 21.5 parts of the crude product obtained were introduced into 215 parts of 86% sulphuric acid and the mixture was stirred for 4 hours at 70–80°C in an atmosphere of nitrogen. The mixture was cooled to room temperature and the sulphuric acid concentration was adjusted to 75% with 31.5 parts of water. The mixture of the sulphates of copper phthalocyanine and copper phthalocyanine carboxylic

acid was filtered, washed with 75% sulphuric acid and then hydrolyzed in 250 parts of water. The pigment was filtered and washed until neutral. For the rearrangement into the β -modification, the moist filter cake was stirred in 200 parts of water, 20 parts of chlorobenzene were added and the mixture was stirred at 100°C for 5 hours. The chlorobenzene was distilled with steam, the aqueous dye suspension was filtered and the filter cake was dried at 100°C.

20 parts of the β -modification of pure copper phthalocyanine were obtained which contained about 8% of copper phthalocyanine carboxylic acid mainly in the form of the copper phthalocyanine monocarboxylic acid.

To bring it into the pigment form, the pure product was ground with 120 parts of acetone and 1200 parts of glass beads having a diameter of 2 mm in a porcelain mill for about 20 hours on a vibration table. The pigment was then isolated and dried at 60°C under reduced pressure. The pigment so prepared is suitable for the colouring of enamels according to known methods in brilliant, greenish blue shades of high degree of purity and high colour intensity. When compared with known commercial products, the pigment of the invention is distinguished by a very good stability to flocculation and an excellent dispersibility in lacquering systems.

When the fine dispersion is carried out with a mixture of 8.4 parts of isobutanol and 111.4 parts of water or a mixture of 60 parts of isopropanol and 60 parts of water as grinding medium instead of 120 parts of acetone, the pigments obtained even after a shorter grinding period have the same quality.

EXAMPLE 2

22.2 parts of unsubstituted crude copper phthalocyanine (in the form of a 90% commercial product) were introduced into 200 parts of 86% sulphuric acid and stirred at 70–80°C for 4 hours in an atmosphere of nitrogen. The copper phthalocyanine sulphate obtained in the form of coarse crystals was filtered, washed with 80% sulphuric acid and hydrolyzed in 250 parts of water. The product was then filtered and washed until neutral. The moist filter cake was introduced into 200 parts of water to convert the α -modification into the β -modification, 20 parts of chlorobenzene were added and the mixture was stirred at 100°C for 5 hours. The chlorobenzene was then removed by steam distillation, the aqueous pigment suspension was filtered and the filter cake dried at 100°C. 20 parts of 100% β -modification of pure copper phthalocyanine were obtained.

For the fine dispersion, the pure pigment obtained and 1.2 parts of copper phthalocyanine - 4 - carboxylic acid were ground with 120 parts of acetone and 1200 parts of

glass beads of 2 mm diameter in a porcelain mill for about 20 hours on a "Vibratom" vibration table. The pigment suspension was then separated from the grinding bodies. The pigment was isolated and dried at 60°C under reduced pressure.

The pigment so obtained colours enamels according to known methods especially brilliant greenish blue shades of a high tinctorial strength and good stability towards flocculation. When compared with known commercial pigments, the pigment of the invention is distinguished by a high degree of purity of shade and an excellent dispersibility in lacquering systems.

The pigment yields in polyvinyl chloride according to known methods colourations of high intensity, a high degree of purity and good dispersibility.

When instead of 120 parts of acetone, 120 parts of methanol or 120 parts of isopropanol or 120 parts of glycolmonomethyl ether or 120 parts of acetic acid - *n* - butyl ester were used as grinding media, pigments of equal quality were obtained. When the fine dispersion is obtained by continuous grinding in a bead mill instead of by vibration grinding, pigments of equal quality were also obtained.

The fine dispersion could also be carried out with equal success by grinding on a roller mill.

EXAMPLE 3

When the 1.2 parts of copper phthalocyanine monocarboxylic acid indicated in Example 2 were replaced by 1.2 parts of copper phthalocyanine - 4,4' - dicarboxylic acid and the grinding and working up carried out as described in Example 2, a pigment was obtained which corresponded to the pigment obtained in Example 2 in respect of its colouristic properties.

EXAMPLE 4

When the 1.2 parts of copper phthalocyanine monocarboxylic acid indicated in Example 2 were replaced by a mixture of 1 part of copper phthalocyanine - 4 - carboxylic acid and 0.2 part of copper phthalocyanine - 4 - carboxylic acid amide and the grinding and working up was carried out as indicated in Example 2, a pigment was obtained which corresponded to that indicated in Example 2 in respect of its colouristic properties.

EXAMPLE 5

20 parts of the β -modification of pure copper phthalocyanine (obtained according to the method described in Example 2) and 2 parts of the sodium salt of copper phthalocyanine - 4 - carboxylic acid were ground together with 120 parts of acetone and 1200 parts of glass beads of 2 mm diameter in a porcelain mill for about 20 hours on a

"Vibratom" vibration table. The pigment was isolated and dried at 60°C under reduced pressure.

The pigment so obtained corresponded to that obtained according to Example 2 with respect to its colouristic behaviour.

When instead of 2 parts of the sodium salt of copper phthalocyanine monocarboxylic acid 2 parts of the barium salt of copper phthalocyanine monocarboxylic acid were used as additive a pigment was obtained which had the same properties.

EXAMPLE 6

32.6 parts of unsubstituted crude CuPc (in the form of a 93% commercial product) were introduced into 300 parts of a 86% sulphuric acid and stirred at 70 to 80°C for 4 hours in an atmosphere of nitrogen. The CuPc-sulphate thus obtained in the form of coarse crystals was filtered after cooling to room temperature, washed with 80% sulphuric acid and then hydrolyzed by introducing the filter cake into 300 parts of water. The copper phthalocyanine was filtered and washed with water until neutral. In order to convert the α -modification into the β -modification, the moist filter cake was introduced into 300 parts of water, 30 parts of chlorobenzene were added and the mixture was boiled under reflux for 4 hours. The chlorobenzene was then removed by steam distillation.

The pigment suspension was filtered and the filter cake was dried at 100°C. 30 parts of the β -modification of pure CuPc were obtained.

For the fine dispersion, the 30 parts of the pure CuPc so obtained were ground after the addition of 1.2 parts of CuPc monosulphonic acid (prepared by sulphonation of CuPc in oleum and having a sulphur content of 5.1%) together with 150 parts of isopropanol and 1200 parts of glass beads of 2 mm diameter in a porcelain mill for 20 hours on a "Vibratom" vibration table. The pigment suspension was then separated from the grinding bodies. The pigment was isolated by filtration and dried at 60°C under reduced pressure.

The pigment so obtained which had a specific surface of about 70 m²/g coloured enamels according to known methods brilliant greenish blue shades of a high degree of purity and tinctorial strength. The pigment was distinguished in comparison with known commercial brands by a good stability towards flocculation and an excellent dispersibility in lacquering systems.

When used in book printing according to known methods, the pigment so obtained yielded prints that were distinguished by high tinctorial strength and an especially high purity of shade.

When the grinding medium used in the fine dispersion was 150 parts of methanol or

150 parts of glycolmonomethyl ether or 120 parts of acetone, instead of the 150 parts of isopropanol, pigments of the same quality were obtained.

- 5 When the additive used for the fine dispersion was 1.5 parts or 1.8 parts of CuPc-monosulphonic acid instead of the 1.2 parts of CuPc-monosulphonic acid, pigments of the same quality were obtained. However, when
10 instead of 1.2 parts of CuPc-monosulphonic acid 3 parts of this compound were used, pigments were obtained which were distinguished in the colouring of lacquers by a very high transparency and an excellent tinctorial
15 strength, but which had low dispersibility.

EXAMPLE 7

- 30 parts of the β -modification of the pure CuPc obtained according to Example 6 and 1.2 parts of CuPc-monosulphonic acid were
20 ground together with 1200 parts of glass beads of 3 mm diameter and a mixture of 139 parts of water and 11 parts of isobutanol in a porcelain mill for 24 hours on a "Vibromat" vibration table. The pigment suspension was then separated from the grinding
25 bodies. The pigment was isolated by filtration and dried at 60°C under reduced pressure.

- When colouring enamels according to known methods, the pigment so prepared yielded brilliant greenish blue shades of a high degree of purity and tinctorial strength. The pigment was distinguished by an excellent dispersibility in lacquers.

- 35 When instead of the mixture of 139 parts of water and 11 parts of isobutanol a mixture of 75 parts of water and 75 parts of isopropanol or a mixture of 112 parts of water and 38 parts of isopropanol was used, pigments were obtained which had the same
40 quality.

- Pigments of the same quality were also obtained when the fine dispersion was not performed discontinuously on a "Vibromat" vibration table, but continuously on a continuous vibration mill or a continuous roller mill.

EXAMPLE 8

- 50 30 parts of the β -modification of the pure CuPc obtained according to Example 6 and 3 parts of the sodium salt of CuPc-monosulphonic acid were ground together with 150 parts of isopropanol and 1200 parts of quartzite beads of 2 mm diameter in a porcelain mill for 24 hours on a "Vibromat" vibration
55 table. The pigment suspension was then separated off from the grinding bodies and the pigment isolated by distilling off the solvent.

- 60 When colouring enamels according to known methods, the pigment so obtained yielded brilliant greenish blue shades of high tinctorial strength. The pigment was distinguished

by a very good dispersibility in lacquers.

Pigments of the same quality were obtained when instead of 3 parts of the sodium salt, 3 parts of the barium salt or 3 parts of the ammonium salt of CuPc-monosulphonic acid were used as additive.

EXAMPLE 9

32.6 parts of unsubstituted crude CuPc (in the form of a 93% commercial product) were introduced into 300 parts of 86% sulphuric acid and then stirred for 4 hours at 70–80°C in an atmosphere of nitrogen. The coarse crystals of CuPc-sulphate so obtained were filtered after cooling to room temperature, washed with 80% sulphuric acid and then hydrolyzed by introducing the filter cake into 300 parts of water. The CuPc was filtered, washed with water until neutral and dried at 100°C. 30 parts of coarse crystals of the α -modification of pure CuPc were obtained.

For the simultaneous rearrangement of the phases and the fine dispersion the α -modification of the pure CuPc was ground after the addition of 1.5 parts of CuPc-monosulphonic acid together with 150 parts of xylene and 1200 parts of glass beads of 3 mm diameter in a porcelain mill for 24 hours on a "Vibromat" vibration table. The pigment suspension was then separated from the grinding bodies. The pigment was isolated by filtration and dried at 60°C under reduced pressure.

The pigment so obtained in the form of the β -crystal modification yielded colourings of high tinctorial strength in enamels. The pigment was distinguished by a very good dispersibility in lacquers.

EXAMPLE 10

95 parts of unsubstituted crude CuPc (in form of a 95% commercial product) and 7.5 parts of CuPc-monosulphonic acid were dissolved together in 1000 parts of 96% sulphuric acid. At 70 to 80°C, 116 parts of water were added dropwise and the suspension was stirred at 70–80°C for 4 hours in an atmosphere of nitrogen. After cooling to room temperature, the CuPc-sulphate was filtered, washed with 80% sulphuric acid and the filter cake was hydrolyzed in 1000 parts of water. 100 parts of chlorobenzene were added to the suspension and the suspension was boiled under reflux for 4 hours. The chlorobenzene was removed by steam distillation. The pigment was isolated by filtration, washed with water until neutral and dried at 100°C.

30 parts of the pure pigment so obtained which was in the form of the β -modification and contained about 6% of CuPc-monosulphonic acid, were ground with 150 parts of isopropanol and 1200 parts of glass beads of 3 mm diameter in a porcelain mill for 24

hours on a "Vibratom" vibration table. The pigment was then isolated by filtration and dried at 60°C under reduced pressure.

- 5 When colouring enamels, the pigment so obtained yielded brilliant greenish blue shades of a high degree of purity and tinctorial strength. The pigment was distinguished by a very good dispersibility in lacquers.

EXAMPLE 11

- 10 30 parts of the β -modification of the pure CuPc obtained according to Example 6 were subjected after the addition of a mixture of 0.9 part of CuPc-monosulphonic acid and 0.3 part of CuPc-disulphonic acid to the process of fine dispersion as described in Example 6.
- 15 The pigment obtained corresponded to that obtained according to Example 6 in respect of its quality.

EXAMPLE 12

- 20 30 parts of the β -modification of the pure CuPc according to Example 6 and 1.5 parts of N,N' - bis(dodecyl) - CuPc - disulphamoyl (prepared by reacting dodecyl amine with the dichloride of CuPc-disulphonic acid) were ground together with 1200 parts of glass beads of 3 mm diameter and 150 parts of acetone in a porcelain mill for 20 hours on a "Vibratom" vibration table. The pigment suspension was then separated from the grinding bodies and the pigment isolated by evaporation.

- When colouring enamels according to known methods the pigment so obtained yielded brilliant greenish blue shades of a high degree of purity and tinctorial strength.
- 35 The pigment was distinguished by an excellent dispersibility.

- When instead of 1.5 parts of the above sulphamoyl additive, a mixture of 1.2 parts of N,N' - bis(isobutyl) - CuPc - disulphamoyl and 0.3 part of N,N',N'' - tris(isobutyl) - CuPc - trisulphamoyl was used as additive, a pigment was obtained which had the same quality.

EXAMPLE 13

- 45 30 parts of the β -modification of the pure CuPc obtained according to Example 6 and 1.5 parts of N,N' - bis(phenyl) - CuPc-disulphamoyl were ground together with 1200 parts of glass beads of 3 mm diameter and 150 parts of isopropanol in a porcelain mill for 24 hours on a "Vibratom" vibration table. The pigment suspension was then separated from the grinding bodies. The pigment was isolated by filtration and dried at 60°C under reduced pressure.

- When colouring enamels, the pigment so obtained yielded brilliant greenish blue shades of a high degree of purity and tinctorial strength. The pigment was distinguished by a very good dispersibility in lacquering systems.
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Pigments of the same quality were obtained, when instead of N,N' - bis(phenyl) - CuPc-disulphamoyl one of the following compounds was used as additive:

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- CuPc - disulphamoyl
N,N' - bis(di-n-butyl) - CuPc-disulphamoyl
N,N' - bis(α -ethylhexyl) - CuPc-disulphamoyl
N,N' - bis(octadecyl) - CuPc-disulphamoyl
N,N' - bis(β -aminoethyl) - CuPc-disulphamoyl and
CuPc - disulphonic acid diphenyl ester
- 70
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EXAMPLE 14

30 parts of the β -modification of the pure CuPc obtained according to Example 6 and a mixture of 1.3 parts of N,N' - bis(di-n-butyl) - CuPc - disulphamoyl and 0.3 part of N,N',N'' - tris(di-n-butyl) - CuPc-trisulphamoyl (prepared by reacting a corresponding mixture of CuPc - disulphochloride and CuPc - trisulphochloride with di-n-butylamine) were ground together with 1200 parts of glass beads of 2 mm diameter, 139 parts of water and 11 parts of isobutanol in a porcelain mill for 24 hours on a "Vibratom" vibration table. The pigment suspension was separated from the grinding bodies, the pigment was isolated by filtration and dried at 60°C under reduced pressure.

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When colouring enamels, the pigment so obtained yielded brilliant shades of a high degree of purity and tinctorial strength.

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When colouring polyvinyl chloride according to known methods, the pigment was easily dispersible and yielded colourations that were distinguished by high tinctorial strength and an extraordinary degree of purity of shade.

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When the fine dispersion was carried out continuously in a bead mill of the type "Molindex" of Messrs. Netzsch with glass beads of 1 mm diameter instead of discontinuously on a vibration table, a pigment was obtained which had the same quality.

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EXAMPLE 15

32.6 parts of unsubstituted crude CuPc (in the form of a 93% commercial product) were introduced into 300 parts of 86% sulphuric acid and stirred for 4 hours at 70—80°C in an atmosphere of nitrogen. The coarse crystals of the CuPc-sulphate so formed were filtered after cooling to room temperature, washed with 80% sulphuric acid and then hydrolyzed by adding the filter cake to 300 parts of water. The CuPc was filtered and washed with water until neutral.

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To rearrange the α -modification into the β -modification, the moist filter cake was added to 300 parts of water, 30 parts of chlorobenzene were then added and the mixture

stirred under reflux for 4 hours. The chlorobenzene was removed by steam distillation. The pigment suspension was filtered and the filter cake was dried at 100°C. 30 parts of the β -modification of pure CuPc were obtained.

For the fine dispersion, the 30 parts of the pure CuPc so obtained were ground after the addition of 3 parts of tris - (isobutylaminomethyl) - CuPc (prepared by reacting tris - (chloromethyl) CuPc with isobutylamine) together with 150 parts of isopropanol and 1200 parts of glass beads of 3 mm diameter in a porcelain mill for 24 hours on a "Vibratom" vibration table. The pigment suspension was then separated from the grinding bodies. The pigment was isolated by filtration and dried at 60°C under reduced pressure.

When colouring enamels according to known methods, the pigment so obtained yielded brilliant greenish blue shades of a high degree of purity and tinctorial strength, and an excellent fastness to light and atmospheric influences. The pigment was distinguished by a good stability towards flocculation and excellent dispersibility in lacquering systems.

When the grinding medium in the fine dispersion process was 150 parts of methanol, 150 parts of glycolmonomethyl ether or 120 parts of acetone instead of the 150 parts of isopropanol, the pigment obtained had the same quality.

The same result was obtained when the fine dispersion was carried out continuously on a continuously operating vibration mill or roller mill instead of discontinuously on a "Vibratom" vibration table.

EXAMPLE 16

30 parts of the β -modification of the pure CuPc prepared according to Example 15 and a mixture of 0.5 part of bis - (isobutylaminomethyl)CuPc, 2 parts of tris - (isobutylaminomethyl) - CuPc and 0.5 part of tetrakis - (isobutylaminomethyl) - CuPc were introduced into 150 parts of isopropanol and stirred until a homogeneous suspension had formed. The suspension was ground continuously on a continuously operating bead mill of the type "Molinox" using glass beads of 1 mm diameter. The pigment was isolated by distilling the solvent. The pigment so obtained corresponded to that obtained according to Example 15 with regard to its quality.

EXAMPLE 17

30 parts of the β -modification of the pure CuPc obtained according to Example 15 and 3 parts of tris - (*n* - octylaminomethyl) - CuPc were ground together with 150 parts of acetone and 1200 parts of quartzite beads of 3 mm diameter in a porcelain mill for 24 hours on a "Vibratom" vibration table. The

pigment suspension was separated from the grinding bodies, the pigment was isolated by filtration and dried at 60°C under reduced pressure.

The pigment so prepared yielded according to known methods enamels of brilliant greenish blue shades of a high degree of purity and tinctorial strength. The pigment was distinguished by a very good dispersibility in lacquers.

Pigments of the same quality were obtained, when instead of tris - (*n* - octylaminomethyl) - CuPc one of the following compounds was used as additive:

tris - (*n* - propylaminomethyl) - CuPc
tris - (*n* - butylaminomethyl) - CuPc
tris - (*n* - hexylaminomethyl) - CuPc
bis - (β - aminoethylaminomethyl) - CuPc
tris - (*n* - dodecylaminomethyl) - CuPc
tris - (*N* - phenylaminomethyl) - CuPc
tris - (*N* - methyl - *N* - phenyl - amino-
methyl) - CuPc

When instead of 3 parts of tris - (*n* - octylaminomethyl) - CuPc only 1.5 parts of this compound were used as additive, a pigment was obtained which also yielded brilliant greenish blue shades of a high degree of purity and tinctorial strength.

EXAMPLE 18

30 parts of the β -modification of the pure CuPc prepared according to Example 15 and 2 parts of tris - (phthalimidomethyl) - CuPc (prepared by reacting CuPc with *N*-methylol-phthalimide in sulphuric acid) were ground together with 1200 parts of glass beads of 3 mm diameter and 150 parts of isopropanol in a porcelain mill for 24 hours on a "Vibratom" vibration table. The pigment suspension was separated from the grinding bodies, the pigment was isolated by filtration and dried at 60°C under reduced pressure.

The pigment so obtained coloured enamels brilliant greenish blue shades of a high degree of purity and tinctorial strength. The pigment was distinguished by an excellent dispersibility in lacquers.

EXAMPLE 19

30 parts of the β -modification of the pure CuPc prepared according to Example 15 and 1.5 parts of tris - (*n* - octylaminomethyl) - CuPc were ground together with 139 parts of water, 11 parts of isobutanol and 1200 parts of glass beads of 2 mm diameter in a porcelain mill for 24 hours on a "Vibratom" vibration table. The pigment suspension was separated from the grinding bodies, the pigment was isolated by filtration and dried at 60°C under reduced pressure.

The pigment so obtained coloured enamels brilliant shades of a high degree of purity and tinctorial strength. When colouring poly-

vinyl chloride according to known methods, the pigment was easily dispersible and yielded colourations of high tinctorial strength which were distinguished by a high degree of purity.

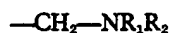
5 When instead of the mixture of 139 parts of water and 11 parts of isopropanol, a mixture of 112 parts of water and 38 parts of isopropanol was used as grinding medium, pigments were obtained that had the same quality.

WHAT WE CLAIM IS:—

1. A process for the manufacture of easily dispersible pigments of the β -modification of a copper phthalocyanine pigment which comprises subjecting the β -modification of a highly pure copper phthalocyanine to mechanical fine dispersion together with a compound of the formula



20 wherein Pc represents a phthalocyanine radical and A represents an identical or different group of the formulae $-\text{COOM}$, $-\text{SO}_2\text{M}$, wherein M represents hydrogen, an alkali metal ion, one molar equivalent of alkaline earth metal or an ammonium ion, or a carbamoyl, sulphamoyl, or N - alkyl carbamoyl group containing 1 to 12 carbon atoms, an N - alkyl - sulphamoyl group containing 1 to 18 carbon atoms, an N,N - dialkyl sulphamoyl group having 1 to 4 carbon atoms in each alkyl group, N - (2 - aminoethyl - sulphamoyl, N - benzyl sulphamoyl, N - (phenylethyl) - sulphamoyl, N - cyclohexylsulphamoyl, N - alkyl N - cyclohexylsulphamoyl having 1 to 4 carbon atoms in the alkyl radical, N - phenyl sulphamoyl, N - alkyl-N - phenyl - sulphamoyl having 1 to 4 carbon atoms in the alkyl radical, carboalkoxy having 1 to 4 carbon atoms in the alkoxy radical, sulphonic acid phenyl ester, sulphonic acid alkyl ester containing 1 to 4 carbon atoms or an aminomethyl group of the formula



45 wherein R_1 represents hydrogen, an alkyl radical having 1 to 18 carbon atoms, 2-aminoethyl, benzyl, phenylethyl, phenyl, alkylphenyl having 1 to 4 carbon atoms in the alkyl radical, alkanoyl having 1 to 4 carbon atoms in the alkyl moiety or benzoyl, R_2 represents hydrogen or an alkyl radical having 1 to 4 carbon atoms, or R_1 and R_2 together represent phthaloyl and

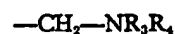
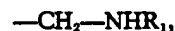
$m=1$ or 2, when A is $-\text{SO}_2\text{M}$, or

55 m =an integer of from 1 to 4, when A is one of said sulphamoyl or sulphonic acid ester groups, or

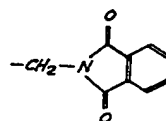
60 m =an integer of from 1 to 3, when A is $-\text{COOM}$ or one of said carbamoyl or carbalkoxy groups, or

m =an integer of from 1 to 6, when A is said aminomethyl group.

2. A process as claimed in Claim 1, wherein A represents COOM or SO_2M , the free acid or the alkali metal, calcium, barium or ammonium salts of said acid groups, sulphamoyl, sulphonic acid phenyl ester, N - alkyl sulphamoyl having 1 to 18 carbon atoms, N,N - dialkyl sulphamoyl having 1 to 4 carbon atoms in each alkyl radical, N - (2-aminoethyl) - sulphamoyl, N - benzyl sulphamoyl, N - (phenylethyl) - sulphamoyl, N - cyclohexyl sulphamoyl, N - alkyl - N - cyclohexyl sulphamoyl having 1 to 4 carbon atoms in the alkyl radical, carbamoyl or aminomethyl of the formula



or



wherein R_1 represents an alkyl radical having 1 to 18 carbon atoms, phenyl or alkylphenyl having 1 to 4 carbon atoms in the alkyl radical, R_3 and R_4 are the same or different alkyl radicals having 1 to 4 carbon atoms;

$m=1$ or 2, when A is $-\text{COOH}$; $-\text{SO}_2\text{M}$ or their salts or carbamoyl;

$m=2$ or 3, when A is one of said sulphamoyl or sulphonic acid ester groups and

90 $m=2$ to 4, when A is one of said aminomethyl groups.

3. A process as claimed in Claim 1 or 2 wherein the amount of the compound of the formula



is within the range of from 2 to 15% by weight calculated on the β -modification of the pure copper phthalocyanine.

4. A process as claimed in any one of Claims 1 to 3, wherein the mechanical fine dispersion process is carried out by grinding in an aqueous-organic or organic grinding medium on a vibrating mill, bead mill or an attritor.

5. A modification of the process as claimed in any one of Claims 1 to 4, wherein the starting material is the α -modification and the phase rearrangement of the β -modification occurs during the mechanical fine dispersion.

6. A process as claimed in any one of Claims 1 to 5, wherein the grinding medium is an aqueous alkanol having 1 to 6 carbon atoms.

7. A process for the manufacture of a phthalocyanine pigment as claimed in Claim 1 conducted substantially as described herein or in any one of the Examples herein.
- 5 8. A process as claimed in Claim 1 wherein any of the starting materials specifically mentioned herein are used.
9. Copper phthalocyanine pigments in the form of the β -modification obtained by the process claimed in any one of Claims 1 to 8.
- 10 10. Copper phthalocyanine pigments as claimed in Claim 1 obtained substantially as described and exemplified herein.
- 15 11. A process for pigmenting articles which comprises contacting said article with a pigment as defined in Claim 9.
12. A process for pigmenting articles which comprises contacting said article with a pigment as defined in Claim 10.
13. A process as claimed in Claim 11 or 12 wherein the article is a lacquer, paper, plastic or a synthetic resin or fibre.
14. A process as claimed in Claim 11 or 12 wherein paper, a textile material, a film or sheet is printed with a pigment as claimed in Claim 9 or 10.
15. A pigmented article, whenever obtained by a process as claimed in any one of Claims 11 to 14.
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